Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for

INFLUENCE OF EXTREME CONDITIONS ON FORMATION AND STRUCTURES OF CAESIUM URANIUM (VI) ARSENATES

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Syntheses of single crystals of $Cs_2[(UO_2)(As_2O_7)]$ (1) at ambient pressure and high temperature conditions. The single crystals of $Cs_2[(UO_2)(As_2O_7)]$ (**1**) were obtained from high-temperature solid-state reactions. The chemicals used were of analytical reagent grade and without any other further purification. The reactants were thoroughly ground together with their appropriate ratios and loaded into a platinum crucible. The initial molar ratios of $CsNO_3$: $NH_4H_2AsO_4$: $UO_2(NO_3)_2 \cdot 6H_2O$ for the syntheses were 1:3:1, 2:7:1, 3:6:1, 4:5:1. The reaction mixture was then placed into a program-controlled furnace (CARBOLITE CWF 1300) and heated up to 800 ^oC at a heating rate of 600 ^oC/h. Afterwards the homogenized melt solution was cooled slowly (5 ^oC/h) down to room-temperature simply by switching off the furnace. All four reaction products consisted of yellow-greenish block-like crystals $Cs_2[(UO_2)As_2O_7]$.

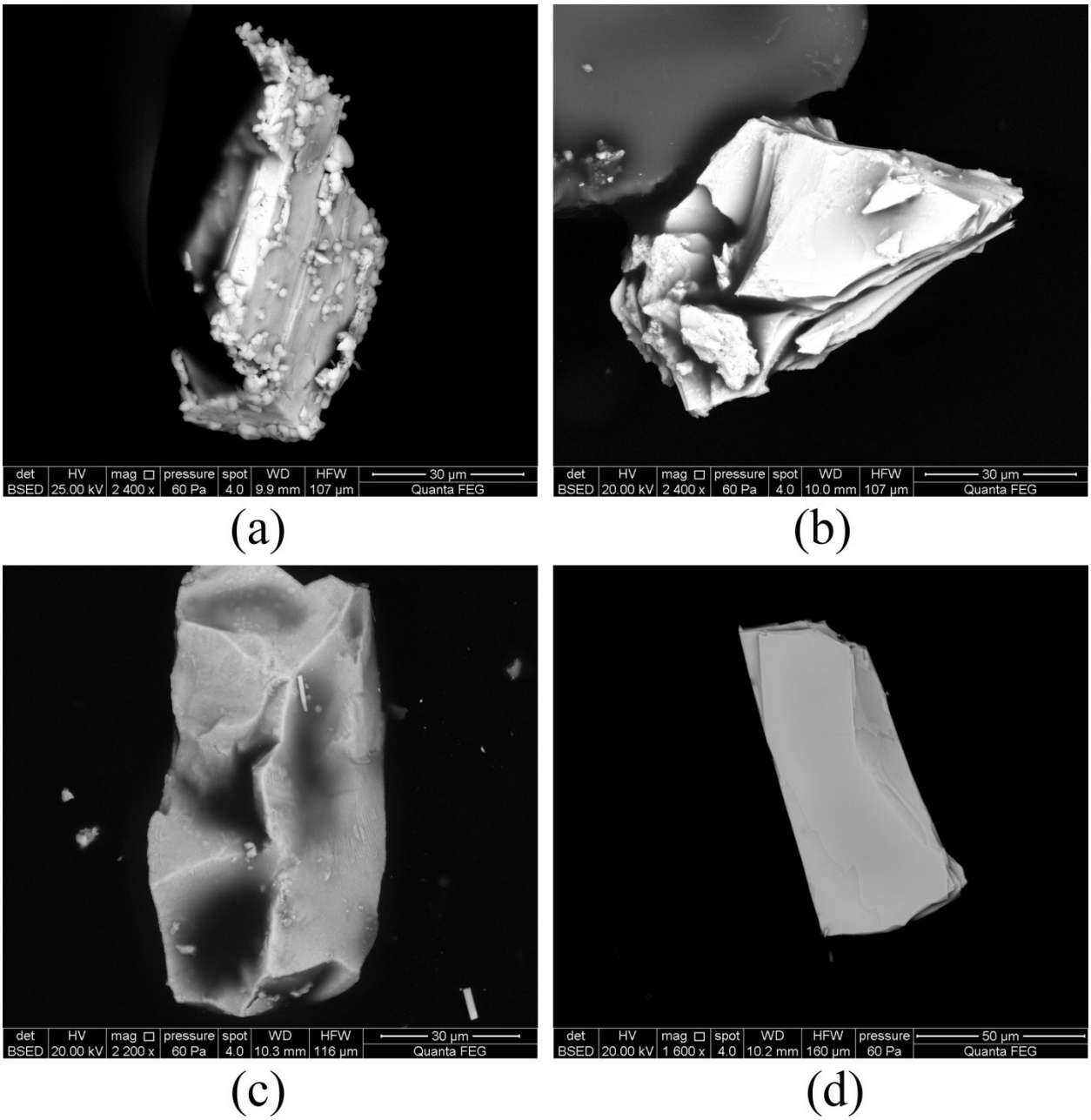

Figure SI1. Electron-microscopic images [(a) to (d)] of $Cs_2[(UO_2)(As_2O_7)]$ (**1**), α-$Cs[(UO_2)(HAs_2O_7)]$ (**2**), β-$Cs[(UO_2)(HAs_2O_7)]$ (**3**), and $Cs[(UO_2)(HAs_2O_7)]\cdot 0.17H_2O$ (**4**), respectively.

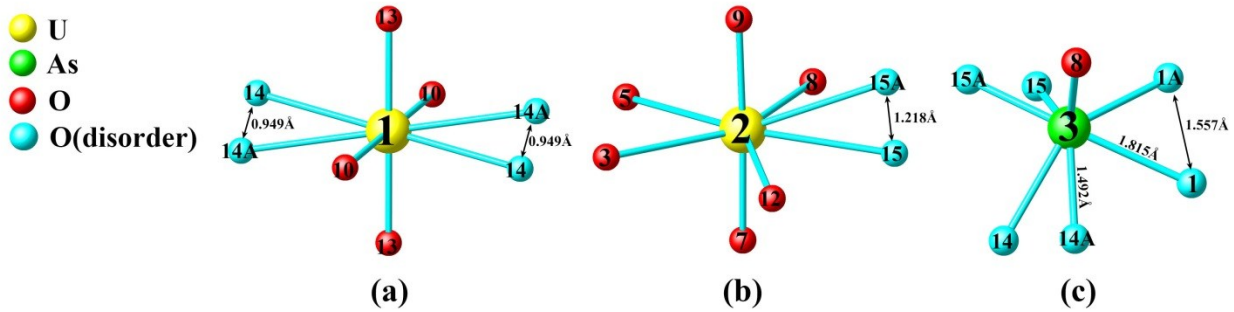

Figure SI2. Local coordination environment of U1, U2, and As3 atoms in compound **3**. The unusual bond lengths of As3–O14A and As3–O1A are indicated by arrows.

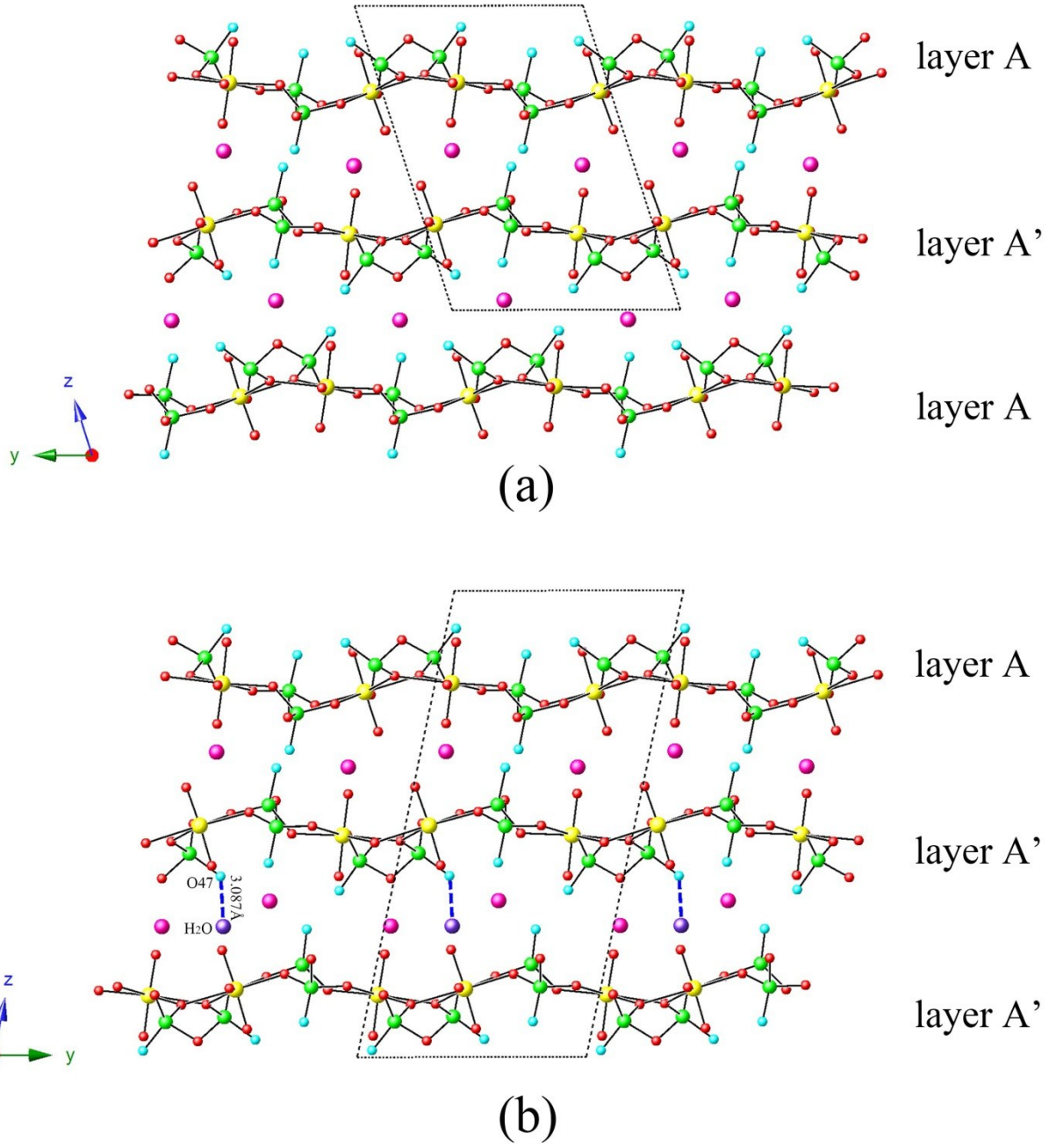

Figure SI3. Ball-and-stick models of layers in (a) compound **2** and (b) compound **4**. U, As, O and Cs atoms are shown as yellow, green (and light blue), red and magenta spheres, respectively, whereas water molecules are shown in purple. Possible hydrogen bonds within the layers are shown as blue dashed lines. Only interlayer hydrogen bonds are marked, whereas hydrogen bonds within the layers are omitted for clarity.

Table SI1: The mass of the reagent used for the synthesis of $Cs_2[(UO_2)(As_2O_7)]$ (**1**), α-$Cs[(UO_2)(HAs_2O_7)]$ (**2**), β-$Cs[(UO_2)(HAs_2O_7)]$ (**3**), and $Cs[(UO_2)(HAs_2O_7)]\cdot 0.17H_2O$ (**4**).

Compound	$CsNO_3$ (g)	As_2O_3 (g)	UO_3 (g)
1	0.034	0.052	0.025
2	0.034	0.104	0.025
3	0.034	0.173	0.025
4	0.013	0.030	0.025

Table SI2: Quantitative amounts of U, As, and Cs (found by EDS and calculated according to chemical formula) in the crystals of $Cs_2[(UO_2)(As_2O_7)]$ (**1**), α-$Cs[(UO_2)(HAs_2O_7)]$ (**2**), β-$Cs[(UO_2)(HAs_2O_7)]$ (**3**), and $Cs[(UO_2)(HAs_2O_7)]\cdot 0.17H_2O$ (**4**), respectively.

Compound \ Element		Cation molar ratio, %			Total, %
		U	Cs	As	
1	experiment	18.9	43.5	37.6	100
	calculated	20	40	40	100
2	experiment	24.7	27.6	47.7	100
	calculated	25	25	50	100
3	experiment	24.7	23.9	51.4	100
	calculated	25	25	50	100
4	experiment	25.8	25.4	48.8	100
	calculated	25	25	50	100

Bond-valence sums (BVS) for all atom positions in $Cs_2[(UO_2)(As_2O_7)]$ (**1**), α-$Cs[(UO_2)(HAs_2O_7)]$ (**2**), β-$Cs[(UO_2)(HAs_2O_7)]$ (**3**), and $Cs[(UO_2)(HAs_2O_7)]\cdot 0.17H_2O$ (**4**) phases were calculated, and the results are given in Table SI3. The bond-valence parameters provided by Burns[1] were used to calculate the U atom and bond-valence parameters provided by Brown and O'Keeffe [2, 3] were used to calculate the As and Cs atom, respectively.

$vu=EXP[(R_0–d)/b]$ ($R_{0(U)}$=2.045 Å, $R_{0(As)}$=1.767 Å, $R_{0(Cs)}$=2.42 Å, $b_{(U)}$=0.51 Å, $b_{(As\ and\ Rb)}$=0.37 Å)

Table SI3a: Bond-valence analysis of $Cs_2[(UO_2)As_2O_7]$ (**1**)

	U1 (50%)	As1 (50%)	As2 (50%)	Cs1 (50%)	Cs2 (50%)	∑
O1 (50%)		1.637		$0.129^{\times 2\downarrow}$	0.198	1.75
O2	$2.286^{\times 2\downarrow}$		$1.676^{\times 2\downarrow}$	$0.082^{\times 2\downarrow}$	$0.064^{\times 2\downarrow}$	2.05
O3 (50%)			1.626	0.140	$0.150^{\times 2\downarrow}$	1.75
O4 (25%)		1.759		0.095		1.12
O5	$2.291^{\times 2\downarrow}$	$1.272^{\times 2\downarrow}$		$0.067^{\times 2\downarrow}$	$0.086^{\times 2\downarrow}$	2.04
O6 (25%)			1.751		0.081	1.13
O7	$1.688^{\times 2\downarrow}$			$0.144^{\times 2\downarrow}$	$0.025^{\times 2\downarrow}$	1.86
∑	5.86	4.99	5.07	1.08	0.93	
(50%) stands for 50% atom site occupation; (25%) stands for 25% atom site occupation						

For compound **1**, not all atom positions are fully occupied. Only O2, O5 and O7 are fully occupied, and only a quarter of O4, O6 is occupied, respectively. All the other atoms are occupied at a rate of 50%. Therefore, here the lack of bond valences of some oxygen atoms isn't a reliable indication for the presence of hydrogen atoms. Only the valence unit of a fully occupied atom is reliable.

Table SI3b: Bond-valence analysis of α-Cs[(UO_2)(HAs_2O_7)] (**2**)

	U1	U2	As1	As2	As3	As4	Cs1	Cs2	∑
	1.715							0.043	1.79
O1								0.035	
	1.691						0.124		1.93
O2							0.119		
		1.721					0.155		1.97
O3							0.095		
		1.705						0.057	1.80
O4								0.036	
O5		0.553	1.300					0.084	1.94
O6*			1.289					0.066	1.36
O7	0.569		1.361				0.142		2.07
			1.008	1.102				0.096	2.26
O8								0.058	
O9*				1.205			0.032		1.24
O10	0.559			1.429				0.066	2.05
O11		0.578		1.265			0.033		1.84
O12	0.420	0.406			1.218				2.08
O13*					1.339		0.118		1.48
O14		0.569			1.269			0.086	1.92
O15					0.927	1.030			1.96
O16	0.399	0.444				1.215	0.035		2.09
O17	0.561					1.350		0.164	2.08
O18*						1.343	0.070		1.41
∑	5.91	5.98	4.96	5.00	4.75	4.94	0.92	0.79	

O* stands for O atom in the OH^- group;

In case of compound **2** all atoms are fully occupied. So, here the lack of bond valence of some O atoms, i.e. O6, O9, O13, and O18, was an indication for the presence of a hydrogen atom.

Table SI3c: Bond-valence analysis of β-Cs[(UO_2)(HAs_2O_7)] (**3**)

		U1 (50%)	U2	As1	As2	As3	Cs1 (50%)	Cs2 (50%)	Cs3 (50%)	∑
O1 (50%)	O1					0.809	0.114			1.00
	O1A					1.105	0.063			1.17
O2 (50%)				1.076						1.08
O3			0.569		1.410					1.98
O4*					1.167				$0.090^{\times 2\downarrow}$	1.26

O5			0.468	1.410					$0.075^{\times 2\downarrow}$	1.95
O6*				1.335			$0.113^{\times 2\downarrow}$		$0.045^{\times 2\downarrow}$	1.49
O7			1.681				$0.070^{\times 2\downarrow}$ $0.097^{\times 2\downarrow}$		$0.042^{\times 2\downarrow}$	1.89
O8			0.566			1.410			$0.112^{\times 2\downarrow}$	2.09
O9			1.681					$0.087^{\times 2\downarrow}$ $0.109^{\times 2\downarrow}$		1.87
O10		$0.623^{\times 2\downarrow}$		1.372				$0.109^{\times 2\downarrow}$		2.11
O11 (50%)					1.076			0.148		1.22
O12			0.469		1.448		$0.071^{\times 2\downarrow}$			1.99
O13		$1.700^{\times 2\downarrow}$						0.041	$0.109^{\times 2\downarrow}$	1.85
O14	O14	$0.701^{\times 2\downarrow}$				1.076		$0.058^{\times 2\downarrow}$		1.84
	O14A	0.572				2.114				2.69
O15	O15		0.605			1.265	$0.091^{\times 2\downarrow}$			1.97
	O15A		0.512			1.372		0.048		1.93
∑		6.07	6.04	5.19	5.10	4.64	1.00	1.01	0.95	

O* stands for O atom in the OH^- group; (50%) stands for 50% atom site occupation; the value with shade background was only sum in the row, not in the column.

For compound **3** the O4 and O6 atoms both sites are fully occupied and the valence unit is 1.26 and 1.49 v.u., respectively. This is a strong indication for the presence of a hydrogen atom.

Table SI3d: Bond-valence analysis for $Cs[(UO_2)(HAs_2O_7)]\cdot 0.17H_2O$ (**4**)

	distance	vu		distance	vu		distance	vu		distance	vu
U1– O53	1.774	1.701	U2– O25	1.768	1.721	U3– O28	1.755	1.766	U4– O22	1.781	1.678
U1– O31	1.754	1.769	U2– O9	1.769	1.718	U3– O15	1.782	1.675	U4– O12	1.779	1.685
U1– O52	2.296	0.611	U2– O38	2.296	0.611	U3– O4	2.303	0.603	U4– O14	2.321	0.582
U1– O41	2.314	0.590	U2– O51	2.328	0.574	U3– O33	2.309	0.596	U4– O1	2.32	0.583
U1– O44	2.356	0.543	U2– O19	2.365	0.534	U3– O27	2.346	0.554	U4– O2	2.346	0.554
U1– O50	2.494	0.415	U2– O50	2.432	0.468	U3– O32	2.495	0.414	U4– O5	2.471	0.434
U1– O49	2.508	0.403	U2– O49	2.469	0.435	U3– O36	2.488	0.420	U4– O11	2.515	0.398
	U1	**6.03**		**U2**	**6.06**		**U3**	**6.03**		**U4**	**5.91**
	distance	vu		distance	vu						
U5– O42	1.741	1.815	U6– O6	1.741	1.815						
U5– O30	1.788	1.655	U6– O10	1.770	1.715						
U5– O17	2.326	0.576	U6– O7	2.300	0.607						
U5– O24	2.337	0.564	U6– O3	2.315	0.589						
U5– O20	2.352	0.548	U6– O8	2.344	0.556						
U5– O32	2.446	0.456	U6– O5	2.476	0.430						
U5– O36	2.470	0.435	U6– O11	2.485	0.422						
	U5	**6.05**		**U6**	**6.13**						

	distance	vu		distance	vu		distance	vu		distance	vu
As1– O7	1.630	1.448	As2– O29	1.618	1.496	As3– O8	1.644	1.394	As4– O18	1.617	1.500
As1– O26	1.624	1.472	As2– O11	1.662	1.328	As3– O16	1.658	1.343	As4– O5	1.687	1.241
As1– O2	1.676	1.279	As2– O1	1.682	1.258	As3– O14	1.662	1.328	As4– O3	1.690	1.231
As1– O23	1.781	0.963	As2– O13	1.755	1.033	As3– O23	1.728	1.111	As4– O13	1.751	1.044
	As1	**5.16**		**As2**	**5.12**		**As3**	**5.18**		**As4**	**5.02**

	distance	vu		distance	vu		distance	vu		distance	vu
As5– O52	1.629	1.452	As6– O20	1.645	1.391	As7– O41	1.640	1.410	As8– O21	1.620	1.488
As5– O19	1.636	1.425	As6– O47	1.664	1.321	As7– O46	1.652	1.365	As8– O4	1.650	1.372
As5– O35	1.646	1.387	As6– O36	1.691	1.228	As7– O50	1.710	1.167	As8– O32	1.691	1.228
As5– O48	1.745	1.061	As6– O40	1.806	0.900	As7– O54	1.799	0.917	As8– O40	1.722	1.129
	As5	**5.32**		**As6**	**4.84**		**As7**	**4.86**		**As8**	**5.22**

	distance	vu		distance	vu		distance	vu		distance	vu
As9– O24	1.656	1.350	As10– O27	1.632	1.440	As11– O38	1.652	1.365	As12– O44	1.645	1.391
As9– O39	1.670	1.300	As10– O17	1.660	1.335	As11– O45	1.663	1.325	As12– O43	1.655	1.354
As9– O33	1.674	1.286	As10– O34	1.679	1.269	As11– O49	1.701	1.195	As12– O51	1.658	1.343
As9– O37	1.743	1.067	As10– O37	1.741	1.073	As11– O54	1.737	1.084	As12– O48	1.760	1.019
	As9	**5.00**		**As10**	**5.12**		**As11**	**4.97**		**As12**	**5.11**

	distance	vu		distance	vu		distance	vu		distance	vu
Cs1– O12	3.090	0.164	Cs2– O4	3.101	0.159	Cs3– O3	3.043	0.186	Cs4– O21	3.171	0.131
Cs1– O10	3.153	0.138	Cs2– O2	3.324	0.087	Cs3– O37	3.276	0.099	Cs4– O25	3.197	0.122
Cs1– O7	3.148	0.140	Cs2– O27	3.344	0.082	Cs3– O20	3.315	0.089	Cs4– OW1	3.203	0.120
Cs1– O29	3.189	0.125	Cs2– O1	3.339	0.083	Cs3– O24	3.313	0.090	Cs4– O41	3.239	0.109
Cs1– O53	3.235	0.111	Cs2– O23	3.342	0.083	Cs3– O23	3.407	0.069	Cs4– O28	3.357	0.079
Cs1– O9	3.247	0.107	Cs2– O26	3.387	0.073	Cs3– O8	3.399	0.071	Cs4– O31	3.386	0.073
Cs1– O46	3.418	0.067	Cs2– O37	3.445	0.063	Cs3– O39	3.415	0.068	Cs4– O30	3.405	0.070
Cs1– O50	3.619	0.039	Cs2– O42	3.462	0.060	Cs3– O22	3.496	0.055	Cs4– O44	3.437	0.064
Cs1– O49	3.638	0.037	Cs2– O15	3.518	0.051	Cs3– O6	3.534	0.049	Cs4– O40	3.601	0.041
Cs1– O16	3.717	0.030	Cs2– O22	3.635	0.037	Cs3– O42	3.666	0.034	Cs4– O50	3.657	0.035
Cs1– O54	3.784	0.025	Cs2– O15	3.664	0.035	Cs3– O6	3.683	0.033	Cs4– O32	3.734	0.029
Cs1– O16	3.808	0.023							Cs4– O48	3.746	0.028
	Cs1	**0.96**		**Cs2**	**0.81**		**Cs3**	**0.84**		**Cs4**	**0.90**

	distance	vu		distance	vu
Cs5– O9	3.082	0.167	Cs6– O30	3.053	0.181
Cs5– O45	3.149	0.139	Cs6– O33	3.105	0.157
Cs5– O53	3.143	0.142	Cs6– O28	3.141	0.142
Cs5– O10	3.176	0.130	Cs6– OW1	3.160	0.135
Cs5– O12	3.270	0.101	Cs6– O35	3.189	0.125
Cs5– O52	3.290	0.095	Cs6– O25	3.175	0.130

Cs5– O18	3.376	0.075	Cs6– O51	3.210	0.118
Cs5– O5	3.642	0.037	Cs6– O47	3.349	0.081
Cs5– O43	3.680	0.033	Cs6– O34	3.558	0.046
Cs5– O11	3.677	0.033	Cs6– O48	3.630	0.038
Cs5– O13	3.799	0.024			
	Cs5	**0.98**		**Cs6**	**1.15**

O1	**1.925**	**O10**	**1.982**	**O19**	**1.959**	**O28**	**1.988**	**O37**	**2.441**	**O46***	**1.432**
O2	**1.920**	**O11**	**2.182**	**O20**	**2.027**	**O29***	**1.621**	**O38**	**1.976**	**O47***	**1.402**
O3	**2.006**	**O12**	**1.949**	**O21***	**1.619**	**O30**	**1.906**	**O39***	**1.368**	**O48**	**2.146**
O4	**2.134**	**O13**	**2.101**	**O22**	**1.770**	**O31**	**1.843**	**O40**	**2.070**	**O49**	**2.071**
O5	**2.141**	**O14**	**1.910**	**O23**	**2.226**	**O32**	**2.126**	**O41**	**2.109**	**O50**	**2.124**
O6	**1.897**	**O15**	**1.761**	**O24**	**2.003**	**O33**	**2.039**	**O42**	**1.909**	**O51**	**2.035**
O7	**2.055**	**O16***	**1.396**	**O25**	**1.974**	**O34***	**1.315**	**O43***	**1.387**	**O52**	**2.159**
O8	**2.022**	**O17**	**1.912**	**O26***	**1.545**	**O35***	**1.512**	**O44**	**1.998**	**O53**	**2.026**
O9	**1.992**	**O18***	**1.575**	**O27**	**2.077**	**O36**	**2.082**	**O45***	**1.464**	**O54**	**2.027**

O* stands for O atom in the OH^- group; OW stands for O atom in the H_2O molecular.

Even for compound **4** all atoms are fully occupied. Here the lack of bond valence of some O atoms is also an indication for the presence of a hydrogen atom. Besides, the sum of valence units for the OW1oxygen atom (see table SI2d above) is 0.255 v.u.. This is clearly a proof for the presence of molecular water in this crystal structure.

References:

1. Burns, P. C., *Can. Miner.,* **1997,** *35*, 1551-1570.
2. Brown, I. D.; Altermatt, D., *Acta Cryst.,* **1985,** *B41*, 244-247.
3. Brese, N. E.; O'Keeffe, M., *Acta Cryst.,* **1991,** *B47*, 192-197.